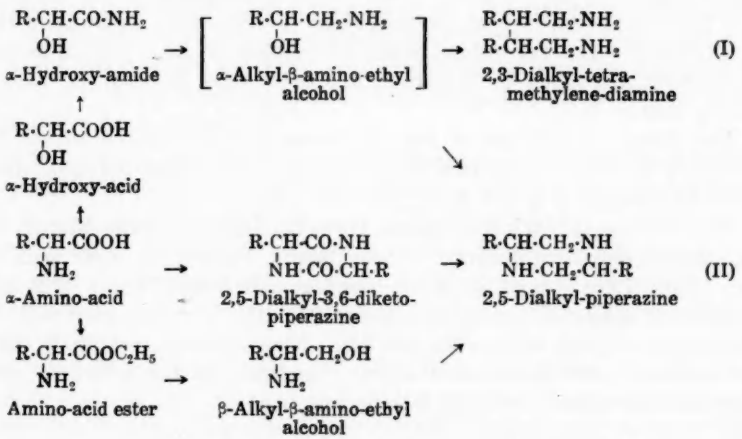
On Some 2,5-Dialkyl-piperazines.[1]

By Haruomi ÔEDA.

(Received June 3, 1938.)

In the previous papers it was described that solid bases were obtained by catalytic hydrogenation of some α-hydroxy-amides and the author concluded that the bases correspond to 2,3-dialkyl-tetramethylene-diamines (I) which would result from further reduction of supposed primary products, α-alkyl-β-amino-ethyl alcohols.



Formula I was given from the facts that the observed molecular weights of the bases were double those of desoxy-amines and that such a condensation of two molecules of amino-alcohols with elimination of two hydroxyls by reduction might probably occur, when deduced in comparison with the work of Rupe and Ackermann.[2] Three kinds of "dialkyl-tetramethylene-diamine" (dimethyl, di-isobutyl and dibenzyl compounds) were mentioned in the previous papers.

After the publication of these papers, the author noticed another possible formula for these bases: i.e. piperazine formula (II). The pipera-

(1) Studies on Hydroxy-acids and Their Derivatives. VII. Correction to V and VI, this Bulletin, **12** (1937), 121, 377.

(2) *Helv. Chim. Acta*, **2** (1919), 221.

zines may be assumed to be formed from two molecules of β-amino-alcohols by dehydration. Similar reactions of alcohols with amines have been observed by many investigators, though a ring formation from β-amino-alcohol leading to piperazine nucleus could not be found as yet described.[3]

The compounds I and II can hardly be distinguished from each other by their analytical results[4] when the radical R is large or the base is analysed in the form of its derivatives. As already described in the previous paper, the author's base is found to behave as a secondary amine in sulphamide reaction. This fact favours formula II for these bases.

Among the three dialkyl-piperazines, the dimethyl and di-isobutyl compounds are known. Dimethyl-piperazine,[5] and its various derivatives are fully described in the literature, while the author's base is isolated in pure state only in the form of its benzoyl compound. Melting points of the benzoyl derivatives of the two bases coincide with each other showing 227–228°. On the other hand, no sufficient data for di-isobutyl-piperazine[6] are given in the literature to discuss its identity with the author's base.

For direct comparison of the two bases in question, the author tried to prepare di-isobutyl-piperazine by reducing the corresponding diketo-piperazine according to the description of Cohn.

Di-isobutyl-piperazine prepared from leucine anhydride was isolated as its hydrochloride (decomp. p. over 330°), though its yield was very poor. Free base (m.p. 80–83°), benzoyl compound (m.p. 222–223°) and benzene-sulphonyl compound (m.p. 211–213°) were prepared. The melting points given above coincide with those of the base and its derivatives isolated from leucic acid amide described in the previous paper. Mixed melting points also prove their identity.

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(3) In some α-amino-aldehydes or α-amino-ketones, similar condensations which result in the formation of dihydro-pyrazine or pyrazine itself, in the presence of some oxidant, are described.

(4) In the previous papers, analytical results of the free bases, hydrochlorides, benzoyl derivatives, etc. are given. Difference of calculated values for the two formulæ in question becomes most notable in case of free bases. Calculated values for the two bases together with observed values are quoted from the previous paper as follows: Di-isobutyl base. Found: C, 72.24; H, 13.66; N, 14.22. Calculated for the piperazine, $C_{12}H_{26}N_2$: C, 72.73; H, 13.25; N, 14.15. Calculated for the tetramethylene-diamine, $C_{12}H_{28}N_2$: C, 71.94; H, 14.09; N, 14.00. Di-benzyl base. Found: C, 80.76; H, 8.54; N, 10.58. Calculated for the piperazine, $C_{18}H_{22}N_2$: C, 81.19; H, 8.35; N, 10.52. Calculated for the tetramethylene-diamine, $C_{18}H_{24}N_2$: C, 80.72; H, 9.02; N, 10.44.

(5) Hoyer, *Z. physiol. Chem.*, **34** (1901), 347.

(6) Cohn, *ibid.*, **29** (1900), 297. The base is isolated and analysed in the forms of its hydrochloride and platinum double chloride. No definite description is found of the free base and other derivatives.

Dibenzyl-piperazine is not found in the literature. Preparation of this base by reducing its diketo compound was unsuccessful, no trace of the piperazine being isolated when phenylalanine anhydride was reduced with sodium in ethyl or amyl alcoholic solution.

By reducing phenylalanine ester with sodium at 160°, Karrer[7] obtained β-benzyl-β-amino-ethyl alcohol, $C_6H_5 \cdot CH_2 \cdot CHNH_2 \cdot CH_2OH$. The preparation[8] was repeated by the present author and the expected amino-alcohol[9] was isolated in two different forms: the one melted at 71–73° and was optically inactive (its monobenzoyl compound, m.p. 148–149°), while the other melted at 92–94° and was optically active, $[\alpha]_D^{23} = -24.4°$ (its monobenzoyl compound, m.p. 169–171°). Besides the amino-alcohol, another solid base which was not described by Karrer, was isolated in a small quantity from the reaction mixture. It showed the same melting point (166–167°) as one of the solid bases[10] resulting from phenyl lactamide as described in the previous paper. Their identity was proved by the mixed melting point tests of the free bases as well as of their benzoyl compounds (m.p. 281–283°).

The amino-alcohol derived from phenylalanine is isomeric with the one which was assumed as an intermediate product in the previous paper, viz., α-benzyl-β-amino-ethyl alcohol, $C_6H_5 \cdot CH_2 \cdot CHOH \cdot CH_2NH_2$. If ring formation by dehydration occurs in these amino-alcohols, they give the same product, 2,5-dibenzyl-piperazine, and in fact, as shown above, the identical solid base was obtained by the reduction of either the hydroxy-amide or the amino-acid ester. This fact indicates that the compound is no doubt dibenzyl-piperazine.[11] The transformation of the amino-alcohols into the piperazine compound by dehydration might be favoured by the reaction temperature as high as 250° in the previous and 160° in the present experiments.

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(7) *Helv. Chim. Acta*, **4** (1920), 97.

(8) Samples of natural leucine and phenylalanine which were the starting materials in the present preparations were the same as used in the preparation of amides of leucic acid and phenyl lactic acid in the previous work.

(9) Karrer isolated this amino-alcohol only in one form of its hydrochloride and no mention was given whether the starting material was active or racemic.

(10) In the previous paper another form of this base (m.p. 150–152°; its benzoyl compound, m.p. 198–200°) was isolated, but in the present experiment it could not be identified.

(11) If the bases resulting from the hydroxy-amide and the amino acid ester were products of further hydrogenation of the amino-alcohols (as considered in the previous paper), their formulæ would be $C_6H_5 \cdot CH_2 \cdot \underset{|}{CH} \cdot CH_2NH_2$ and $C_6H_5 \cdot CH_2 \cdot CH(NH_2) \cdot \underset{|}{CH_2}$
$C_6H_5 \cdot CH_2 \cdot \underset{|}{CH} \cdot CH_2NH_2$ $C_6H_5 \cdot CH_2 \cdot CH(NH_2) \cdot \underset{|}{CH_2}$.
They are isomeric with each other but never identical.

These considerations lead the author to conclude that 2,5-dialkyl-piperazine formulæ, instead of dialkyl-tetramethylene-diamine formulæ, are to be given to the solid bases described in the previous papers.

Experimental.

2,5-Di-isobutyl-3,6-diketo-piperazine (Leucine Anhydride.) Prepared from natural leucine by heating at 170° in the presence of glycerine.[12] M.p. 263° (uncorr.) or 270° (corr.) after recrystallisation from alcohol.

Reduction of Leucine Anhydride. The anhydride (10 g.) was added to absolute alcohol (dehydrated with metallic sodium, 500 c.c.). It dissolved completely when the mixture was kept boiling. Large excess of sodium (30 g.) was added to the boiling solution in small pieces through reflux condenser in the course of half an hour. After cooling, an equal volume of water was added and the alcohol was removed in vacuum. When the volume of the residue diminished to nearly half of the initial, the distillation was stopped. After removing precipitated unreacted anhydride, the filtrate was extracted with a large bulk of ether. After drying over caustic soda, ether was expelled from the extract and a little anhydride again crystallised out. Total yield of recovered anhydride corresponded to more than 10%, even when large excess of sodium was used. The residue (2.5 g.), after separation of the crystals, was distilled under reduced pressure through Widmer column and was separated into two fractions:

(I)	up to 100°	under 6 mm.	0.5 g.
(II)	over 100°	,,	1.2 g.

Fraction II tended to solidify in the receiver, while fraction I remained as viscous fluid. Both of the fractions were dissolved in ether separately and were extracted with dilute hydrochloric acid. From fraction I a hydrochloride very soluble in water was isolated, while from fraction II another hydrochloride insoluble in water was obtained together with the above soluble one.

Hydrochloride, Soluble in Water (a Base Left Undetermined). Crude sample from fraction I weighed 0.25 g. After decolouration with charcoal it crystallised from alcohol in colourless leaflets. The combined yield of pure sample from both fractions was 125 mg. M.p. 160–162° (uncorr.). No study on this hydrochloride was made.

Hydrochloride, Insoluble in Water (2,5-Di-isobutyl-piperazine). Crude sample weighed 0.2 g. After washing with alcohol it was dissolved in a large volume of hydrochloric acid and, after decolouration with charcoal, the solution was evaporated on the water bath. Colourless hydrochloride crystallised out while still hot before the solution completely dried up. It weighed 168 mg. Decomp. p. over 330°.

Free base. When the pure hydrochloride (50 mg.) was warmed with dilute caustic soda, free base separated out as an oil and turned to crystals on cooling. The separated base was dissolved in alcohol and filtered. After evaporation to a small

(12) Maillard, *Ann. chim.*, [9]. **3** (1915), 83.

bulk, the free base was crystallised by adding water. M.p. 80–83°[13] after drying over caustic soda.

Benzoyl compound. The pure hydrochloride (33 mg.) was added to dilute caustic soda (2 c.c.) and benzoyl chloride was added drop by drop. Benzoyl compound was formed as sticky mass and turned to crystals on shaking. M.p. 217–218° (uncorr.) or 222–223° (corr.) after one recrystallisation from alcohol. No depression of melting point was observed when mixed with the sample described in the previous paper. (Benzoyl compound of the solid base from leucic acid amide melted at 223–224° (corr.) and its analytical result was given in the previous paper.)

Benzene-sulphamide. To a suspension of the free base in dilute caustic soda (50 mg. of the hydrochloride in 1 c.c.) benzene-sulphonyl chloride (2 drops, nearly equivalent) was added. Crude sulphamide (70 mg.) separated out as crystals. After recrystallisation from alcohol, it (39 mg.) melted at 206–208° (uncorr.) or 211–213° (corr.), alone or mixed with the sample described below. (Found: N, 5.69. Calculated for $C_{12}H_{24}N_2(C_6H_5SO_2)_2$: N, 5.85%.)

Benzene-sulphamide of "solid base from leucic acid amide". From the free base melting at 62–64° (50 mg.) and benzene-sulphonyl chloride (3 drops), crude sulphamide (78 mg.) was obtained just in the same way as above. When recrystallised from alcohol, the purified sample (19 mg.) melted at 205–207° (uncorr.) or 210–212° (corr.) and it was used in the above mixed melting point test.

Ethyl Ester of Phenylalanine. Prepared from natural phenylalanine and alcohol by dehydration with gaseous hydrochloric acid.[14] B.p. 135–136° under 8 mm.

Reduction of Phenylalanine Ester. Metallic sodium (45 g.) cut in small pieces was placed in a litre-flask which was immersed in an oil bath (160°). Mixture of the ethyl ester of phenylalanine (38 g.) and absolute alcohol (120 c.c.) was added drop by drop to the sodium through reflux condenser in the course of one hour. After interval of half an hour, a new bulk of alcohol (150 c.c.) was added and then the oil bath was detached. Alcohol was again poured until the metallic sodium completely disappeared. After cooling, water was added to dissolve separated alcoholate. The alcohol was removed in vacuum at 50–70° and the residue was concentrated also in vacuum until a light coloured oil separated in the flask.

The oil (not miscible with ether) and the water layer were separately extracted with a large bulk of ether. From the combined extract, after dehydration with sodium sulphate, ether was removed and the residue was concentrated to a small bulk on boiling water bath. Small amount of crystals gradually deposited on standing.

Dibenzyl-piperazine. The crystals were separated and washed with a little ether. After recrystallisation from alcohol, it melted at 163–164° (uncorr.) or 166–167° (corr.) and the sample amounted to 0.45 g. No depression of melting point was observed when the base was mixed with the base resulting from phenyl lactamide (m.p., the same; its analytical result was given in the previous paper).

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(13) Solid base isolated from leucic acid amide, as already mentioned, shows different melting points 62-64° and over 80°). They are identical in analytical result and may be presumed to be mixtures of isomers. But their differentiation in the form of derivatives was unsuccessful.

(14) Fischer and Schöller, *Ann.*, **357** (1907), 1.

Benzoyl compound. Prepared from the above base (50 mg.) and benzoyl chloride (180 mg.) in alkaline medium (1.5 c.c. of 2N caustic soda). Crude benzoyl compound (79 mg.) separated, after washing with hot alcohol, was once recrystallised from glacial acetic acid. M.p. 274–276° (uncorr.) or 281–283° (corr.), alone or mixed with the benzoyl compound of the base resulting from phenyl lactamide (m.p., 280–282°; its analytical result was given in the previous paper).

β-Benzyl-β-amino-ethyl alcohol. After removal of dibenzyl-piperazine, the remaining syrup was subjected to vacuum distillation. The part distilling at 147–151° under 10 mm. was collected. It amounted to 4.4 g. and was colourless viscous fluid tending to crystallise after long standing. The crystals, after washing with a little benzene, on heating, softened at 65–70° and melted below 75°. By fractional recrystallisation from benzene it could be separated into two fractions. The part less soluble in benzene (1.27 g.) melted at 91–93° (uncorr.) or 92–94° (corr.) (Found: C, 71.63; H, 9.31;[15] N, 9.10%), $[\alpha]_D^{23} = -24.4°$ (28.25 mg. in 1.00 c.c. alcoholic solution; $l = 1$ dm.; $\alpha_D^{23} = -0.69°$). The part more soluble in benzene (0.94 g.) melted at 70–72° (uncorr.) or 71–73° (corr.) (Found: C, 71.78; H, 9.04; N, 9.29. Calculated for $C_9H_{13}ON$: C, 71.45; H, 8.67; N, 9.26%), $[\alpha]_D^{23}$ = almost null (−0.35°) (28.55 mg. in 1 c.c. alcoholic solution; $l = 1$ dm.; $\alpha_D^{23} = -0.01°$).

Benzoyl compound. The unfractionated mixture of the base (200 mg.) was dissolved in 2N caustic soda (6 c.c.) and benzoyl chloride (500 mg.) was added drop by drop with constant shaking. Crude benzoyl compound (250 mg.) separated could be differentiated into two fractions by fractional recrystallisation from benzene-alcohol (1:1). They were found, on analysis, to be mono-benzoyl derivatives. The part less soluble in the solvent (40 mg.) melted at 166–168° (uncorr.) or 169–171° (corr.) (Found: C, 75.34; H, 7.29; N, 5.45%). The more soluble part (51 mg.) melted at 146–147° (uncorr.) or 148–149° (corr.) (Found: C, 75.25; H, 7.14; N, 5.42. Calculated for $C_9H_{12}ON(C_6H_5CO)$: C, 75.25; H, 6.72; N, 5.49%).

The two forms of the benzoyl compound could be prepared from the fractionated free bases; the base with higher melting point giving the derivative with higher melting point and the lower one giving that with lower melting point.

In conclusion, the author expresses his sincere thanks to Mr. R. Suzuki, Director of the factory, for every facility given to the author and also to Dr. Y. Takayama for constant encouragements.

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(15) Determinations of carbon and hydrogen and measurements of optical rotation in this paper were done by Mr. Toshio Ando, to whom the author is very grateful.

Absorption Spectra of Co-ordination Compounds. III. Special Bands of Chromium Complexes.

By Ryutaro TSUCHIDA and Masahisa KOBAYASHI.

(Received June 16, 1938.)

It has been established by extensive studies of Y. Shibata[1] and his co-workers that the metallic complex has generally two absorption bands, of which the first appears usually in the visible region and the second in most cases in the ultra-violet. One of the present authors[2] has recently come to the conclusion that the first band is attributed to electron transitions in unsaturated transition shells of the central ions and the second band may be explained as due to a kind of incomplete dissociation of the complex radical brought about by irradiation, during which the co-ordinate bond is temporarily broken and the ligand is converted into an excited ion or molecule remaining in general in its seat of co-ordination. Moreover, some complexes may have the third bands[3] which are due to negative ligands co-ordinated in trans-positions to each other.[4] It has been postulated by the present author[5] that the third band is originated in a kind of neutralization between the central ion and one of the co-ordinated anions, during which the ligand is converted into an ionogen which recombines in most cases to regenerate the original complex.

According to the trans-anion hypothesis, $[Cr(NH_3)_5NCS](NCS)_2$ could not be expected to have a third band, nevertheless it shows three absorption bands in aqueous solutions[6] as well as in liquid ammonia.[7] Since rhodanate ion has no absorption band in the spectral regions in question when it is not co-ordinated, Y. Shibata[8] has explained the extra band of the rhodanato-complex as due to NCS-radical combined to the central metallic atom. Uzumasa, Okuno and Doi[9] have recently

(1) Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, 1915 to 1921; *J. Chem. Soc. Japan*, 1915 to 1922.

(2) R. Tsuchida, this Bulletin, **13** (1938), 388.

(3) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1243.

(4) R. Tsuchida, this Bulletin, **11** (1936), 721.

(5) R. Tsuchida, this Bulletin, **13** (1938), 436.

(6) Y. Shibata and K. Matsuno, *J. Chem. Soc. Japan*, **39** (1918), 661; Y. Shibata, *J. Coll. Sci., Imp. Univ. Tokyo*, **41** (1918), Art. 6.

(7) H. Shiba and T. Inoue, *J. Chem. Soc. Japan*, **56** (1935), 213.

(8) Y. Shibata, *J. Chem. Soc. Japan*, **35** (1914), 807.

(9) Y. Uzumasa, H. Okuno, and K. Doi, *J. Chem. Soc. Japan*, **59** (1938), 655.

illustrated the hypothesis by absorption bands of a number of rhodanates. Such bands are due to ligands themselves and, therefore, could be attributed neither to transition electrons of the central atom nor to co-ordination electrons of the co-ordination center in question. Being thus unable to be classified as any of the numbered bands, they are described here as special bands.

The present paper deals with some of such special bands taking chromium compounds as examples and also refers to the relation between absorption spectra and chemical properties.

Experimental.

The chromium complexes were prepared as described below and their absorption spectra in aqueous solutions were observed. The molar extinction coefficient ε is given by Beer-Lambert's law: $I = I_0 \times 10^{-\varepsilon cd}$, where c is the concentration in gram-ion per liter and d the thickness of the layer in cm. The absorption curves are given in Tables 1, 2 and 3.

$[Cr(H_2O)_6]Cl_3$ was prepared by the method of Bjerrum.[10] Spectrographic measurements: $c = 0.1$ mol/l. and $d = 15.0$ to 0.30 cm. The measurements were carried out at 20°C., as the complex undergoes tautomeric change at higher temperatures.

$[Cr(NH_3)_6]Cl_3$ was prepared by the method of Christensen[11] from anhydrous chromic chloride and liquid ammonia. Freshly prepared chromic chloride gives better yield of the luteo-salt. Spectrographic measurements: $c = 0.01$ mol/l. and $d = 5.00$ to 1.05 cm.

$[Cr(NH_3)_5Cl]Cl_2$ was partly prepared by the method of Christensen[11] and partly by our own. By introducing anhydrous chromic chloride in liquid ammonia the purpureo-salt and the luteo-complex are simultaneously produced, but of freshly prepared chromic chloride most portion is converted into the hexammine complex. The present authors heated hydrated chromic nitrate $Cr(NO_3)_3 \cdot 9H_2O$ with liquid ammonia at about 50°C. for a few hours in an autoclave. Excess of ammonia was evaporated and the residue was then treated with hydrochloric acid. Crude pentammine salt thus obtained was purified as usual. Spectrographic Measurements: $c = 0.005$ mol/l. and $d = 15.0$ to 1.05 cm.

$[Cr(NH_3)_5NCS](NCS)_2$. Werner and Halban[12] reported that they were unable to prepare the rhodanato-complex in crystalline form

(10) N. Bjerrum, *Z. physik. Chem.*, **59** (1907), 340.
(11) O. T. Christensen, *Z. anorg. Chem.*, **4** (1893), 229.
(12) A. Werner and J. v. Halban, *Ber.*, **39** (1906), 2669.

and it was still impure after second recrystallization. The colour according to the same authors is reddish brown to orange and their analysis gave 18.27% Cr for the theoretical value of 16.7% Cr.

The present authors prepared the salt by the same method and obtained it in two different crystalline forms after repeated recrystallization: yellowish pink crystalline powder and brownish red pyramidal crystals of about 1 mm. in length. The two forms are usually obtained as mixtures in various proportions according to conditions in recrystallization, and consequently the colour may be sometimes reddish brown and sometimes orange as has been described by Werner and Halban. Rapid precipitation from hot solutions gives yellowish pink form and slow crystallization from cold solutions the brownish red form. The chromium contents of the two forms were found to be 16.3% and 15.9% respectively, corresponding to theoretical values of 16.7% as $Cr(NCS)_3 \cdot 5NH_3$ and 15.8% as $Cr(NCS)_3 \cdot 5NH_3 \cdot H_2O$. The absorption of both the forms was measured. Spectrographic measurements: $c = 0.002$ mol/l. and $d = 15.0$ to 0.08 cm. The absorption curves thus obtained were identical, showing that the water molecule in the reddish brown form is merely the water of crystallization outside the complex radical.

$[Cr(NH_3)_2(NCS)_4]NH_4 \cdot H_2O$ was prepared by the method of Christensen.[13] Spectrographic measurements: $c = 0.001$ mol/l. and $d = 15.0$ to 0.04 cm.

$[Cr(NCS)_6]K_3 \cdot 4H_2O$ was prepared by the method of Roesler.[14] Spectrographic measurements: $c = 0.001$ mol/l. and $d = 15.0$ to 0.04 cm.

$[Co(NH_3)_5CrO_4]Cl$ was prepared by the method of Briggs.[15] Spectrographic measurements: $c = 0.001$ mol/l. and $d = 5.00$ to 0.02 cm.

K_2CrO_4. Spectrographic conditions: $c = 0.010$ and 0.002 mol/l. and $d = 1.05$ to 0.02 cm.

Discussion of the Results.

(1) Special Bands of Rhodanato-complexes. Whereas $[Cr(H_2O)_6]Cl_3$, $[Cr(NH_3)_6]Cl_3$ and $[Cr(NH_3)_5Cl]Cl_2$ have two bands each, the first and the second, $[Cr(NH_3)_5NCS](NCS)_2$ has three and $[Cr(NH_3)_2(NCS)_4]NH_4$ and $[Cr(NCS)_6]K_3$ have four bands each, just as could be expected from the author's hypotheses.[2][5]

As is clear from Fig. 1 and Table 1, substitution of NCS^- for NH_3 is bathochromic and at the same time hyperchromic for the first and the second band. Then the same substitution must be bathochromic also for

(13) O. T. Christensen, *J. prakt. Chem.*, **45** (1892), 216.
(14) J. Roesler, *Ann.*, **141** (1867), 185.
(15) S. H. C. Briggs, *J. Chem. Soc.*, **115** (1919), 70.

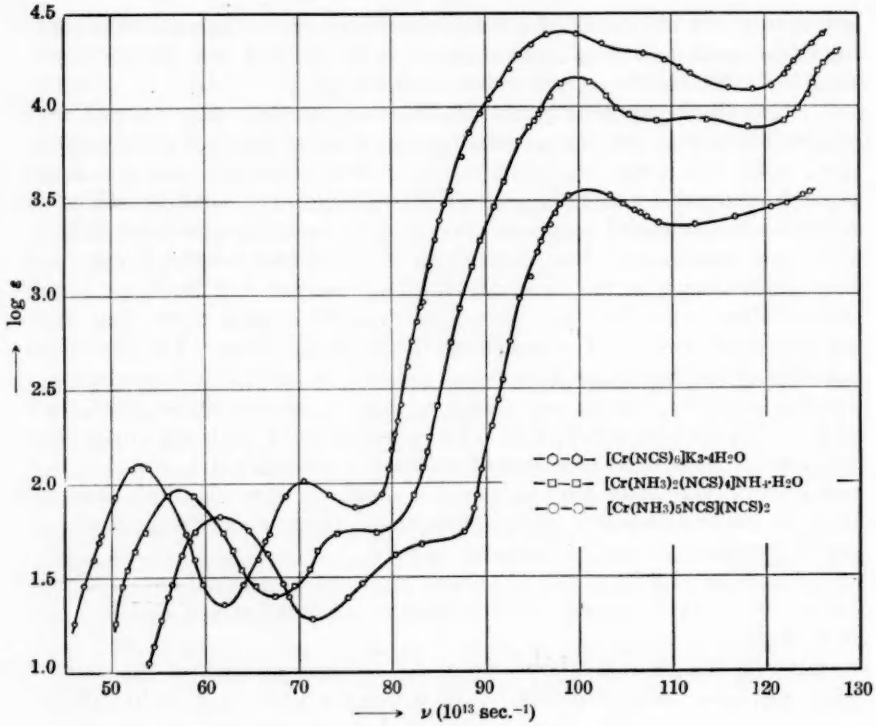

Fig. 1.

Table 1.

Complex compounds	1st bd.		2nd bd.		Special bd.		3rd bd.	
	$\nu_1(10^{13})$	log ε	$\nu_2(10^{13})$	log ε	$\nu_s(10^{13})$	log ε	$\nu_3(10^{13})$	log ε
$[Cr(NH_3)_5NCS](NCS)_2$	61.5	1.82	(83)	1.67	100.4	3.56		
$[Cr(NH_3)_2(NCS)_4]NH_4$	57.5	1.95	(75)	1.75	99.6	4.17	(113)	3.9
$[Cr(NCS)_6]K_3$	53.1	2.08	70.8	2.00	98.6	4.40	(108)	4.3
$[Co(NH_3)_5NCS]Cl_2$ [16]	60.2	2.14	(84)	2.60	98.0	3.20		
[Co dg'_2 NH_3Cl] [17]	63.8	1.75	86.0	3.08	(101)	3.7	121.8	4.50
[Co dg'_2 *py* Cl] [18]	65.5	2.24	89.0	3.39	(102)	3.7	121.5	4.35

(16) R. Tsuchida, *J. Chem. Soc. Japan*, **59** (1938), 592.
(17) R. Tsuchida and M. Kobayashi, this Bulletin, **12** (1937), 83. The symbol dg' denotes a dimethylglyoxime residue behaving as a monobasic acid.
(18) S. Kashimoto and M. Kobayashi, this Bulletin, **12** (1937), 350. The symbol *py* denotes a pyridine molecule.

the third band, so long as the following relation[5] should exist between the second and the third band.

$$h\nu_3 - h\nu_2 = P + E - J = \text{constant.}$$

For $[Cr(NH_3)_2(NCS)_4]NH_4$ and $[Cr(NCS)_6]K_3$, therefore, the third bands are those of the shortest wave-lengths. The band at about 100×10^{13} sec.$^{-1}$ which remains almost unaffected by the substitution is the special band due to Cr←N=C.

It is interesting to notice that the ε-value of the special band is approximately proportional to the number of NCS-radicals in the co-ordination. This fact shows that the special band is additive and the

Table 2.

Rhodanato-complexes	$\nu_a(10^{13}\text{sec.}^{-1})$	log ε	ε	Ratio
$[Cr(NH_3)_5NCS](NCS)_2$	100.4	3.56	36×10^2	1
$[Cr(NH_3)_2(NCS)_4]NH_4$	99.6	4.17	15×10^3	4
$[Cr(NCS)_6]K_3$	98.6	4.40	25×10^3	6.6

additivity in turn suggests that the absorption centers of the special band in a complex radical are fairly independent with one another, which could not be the case for the other numbered bands.

Whereas the second band of $[Cr(NCS)_6]K_3$ is isolated from the special band, those of $[Cr(NH_3)_2(NCS)_4]NH_4$ and $[Cr(NH_3)_5NCS](NCS)_2$, however, are partly superposed by their special bands. Further the second band of $[Co(NH_3)_5NCS]Cl_2$[16] is inexplicit, being almost entirely covered by its special band, which is due to the origin similar to that in the cases of rhodanato-chromic complexes. It has been shown by Shibata[19] that $[Co(NCS)_4]K_2$ has also a special band of similar origin. A peculiar group which may be represented by M←N=C is the common feature of all the above-mentioned complexes which have the special bands. Thus the special bands of $[Co\,dg_2'\,NH_3\,Cl]$[17] and $[Co\,dg_2'\,py\,Cl]$[18] might also be explained as due to the same group of M←N=C. In Table 1 are summarized the complexes which have the special bands due to M←N=C, where M is a metallic ion of any valency and of any kind, perhaps including hydrogen ion as in free thiocyanic acid.

(19) Y. Shibata, *J. Chem. Soc. Japan*, **35** (1915), 807; A. Hantzsch and Y. Shibata, *Z. anorg. Chem.*, **73** (1912), 309.

(2) Special Bands of Chromato-pentammine Cobaltic Salt. Being due to the unsaturated transition shell of the central ion, the first band[2] is expected for all the tervalent chromium complexes. For chromate ion, however, the first band could not be expected, as it has an electronic configuration similar to that of sulphate ion. The second and the third band are expected from the consideration given in the preceding paper[5] and are found at 81×10^{13} sec.$^{-1}$ and 110×10^{13} sec.$^{-1}$ respectively. The absorption curve is given in Fig. 2.

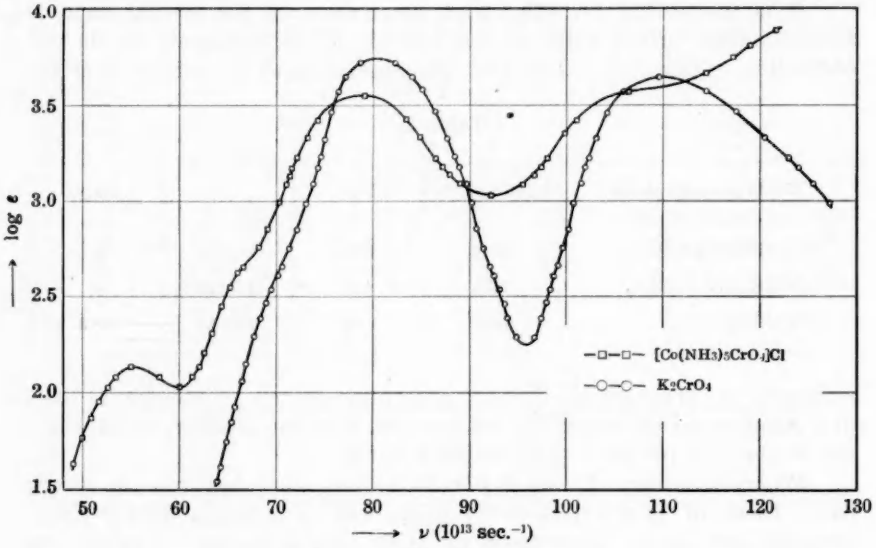

Fig. 2.

The absorption spectrum of $[Co(NH_3)_5CrO_4]Cl$ may be analysed into spectra mainly due to a sexa-coördinate absorption unit whose center is Co and a quadri-coördinate unit whose center is Cr. These absorption units may be denoted as $[(NH_3)_5Co–O–]$ and $[–O–CrO_3]$ for the sake of convenience. These two units are combined with each other having one oxygen atom in common. The former should have two bands, the first and the second, and the latter also two bands, the second and the third. As can be seen from Fig. 2, the absorption bands due to $[–O–CrO_3]$ are slightly shifted towards the longer wave-lengths compared with those of free CrO_4^- alone and the extinction coefficients at the absorption maxima of the former are considerably smaller than those of the latter: in other words, formation of co-ordinate linkage between Co^{+++} and CrO_4^- has a

bathochromic and a hypochromic effect upon the absorption bands of CrO_4^-. The first band of $[(NH_3)_5Co–O–]$ is at 55.6×10^{13} sec.$^{-1}$, but the second band is completely covered by the strongly absorbing second band of $[–O–CrO_3]$.

The bands of $[–O–CrO_3]$ in this case may be regarded as special bands of $[Co(NH_3)_5CrO_4]Cl$, if we take Co as the center of the entire complex. If we take Cr as the center, the bands of $[(NH_3)_5Co–O–]$ may be regarded as special bands as well. The special band, therefore, is relative to the absorption unit in question, and is essentially a numbered band of some other absorption unit.

We may notice that there are two kinds of special bands: viz., the bands which may be observed in the ligands themselves even when they are not combined in co-ordination and those which appear only when the ligands are co-ordinated. The special bands of the first kind may be represented by $[Co(NH_3)_5CrO_4]X$ and those of the second kind may be illustrated by $[Cr(NH_3)_5NCS]X_2$, etc.

(3) Stability and Absorption Spectra of Chromic Complexes. All the co-ordination compounds which contain tervalent chromium ions should

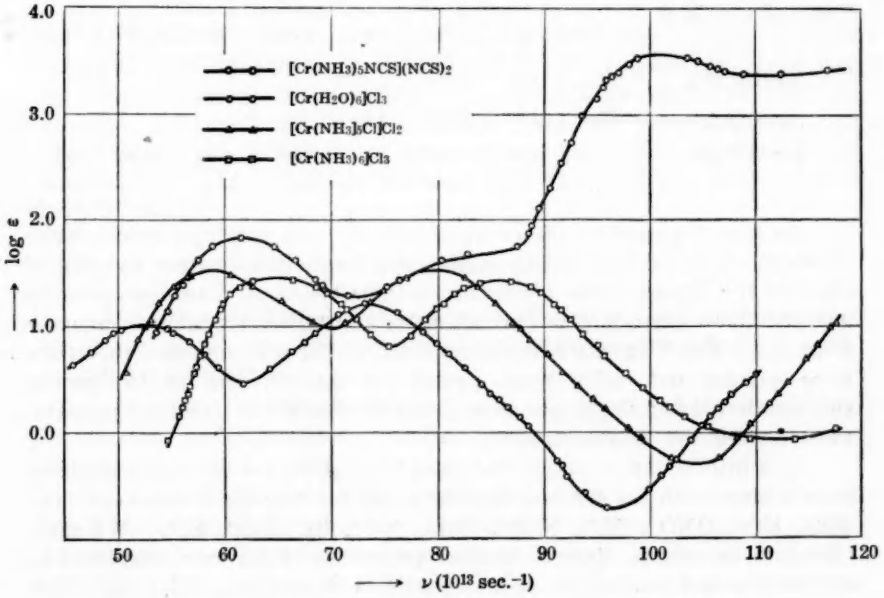

Fig. 3.

have the first and the second bands, the latter giving the measure of stability.[5] From the chromic complexes in Figs. 1 and 3, we may be able to find the spectrochemical series of ligands. Thus the hypsochromic order of ligands for the second bands of chromic complexes is NH_3, NCS^-, Cl^-. (Table 3). The hypsochromic order is from Table 4 NH_3, H_2O, NCS^-. Combining both series, we obtain NH_3, H_2O, NCS^-, Cl^-.

Table 3.

Chromic complexes	1st bd.		2nd bd.		Special bd.	
	$\nu_1(10^{13})$	log ε	$\nu_2(10^{13})$	log ε	$\nu_s(10^{13})$	log ε
$[Cr(NH_3)_5NH_3]Cl_3$	65.0	1.48	86.0	1.44		
$[Cr(NH_3)_5NCS](NCS)_2$	61.6	1.82	(83)	1.67	100.4	3.56
$[Cr(NH_3)_5Cl]Cl_2$	58.7	1.53	80.0	1.54		

Table 4.

Chromic complexes	1st bd.		2nd bd.		Special bd.		3rd bd.	
	$\nu_1(10^{13})$	log ε	$\nu_2(10^{13})$	log ε	$\nu_s(10^{13})$	log ε	$\nu_3(10^{13})$	log ε
$[Cr(NH_3)_6]Cl_3$	65.0	1.48	86.0	1.44				
$[Cr(H_2O)_6]Cl_3$	52.5	1.02	73.6	1.20				
$[Cr(NCS)_6]K_3$	53.1	2.08	70.8	2.00	98.6	4.40	(108)	4.3

As was discussed in the previous paper,[5] the spectrochemical series shows the order of the stability of the co-ordinate link between the central ion and the ligand. The above series indicates that chloro-pentammine and rhodanato-pentammine chromic salts are rather unstable in aqueous solutions. The absorption measurements of these complexes, therefore, were carried out with great precaution against the photo-chemical aquotization, using the solutions as fresh as possible by frequent preparations during the measurements.

It is interesting to notice that the above series for chromic complexes is coincident with the spectrochemical series for cobaltic complexes,[5] i.e., NH_3, NO_2^-, ONO^-, H_2O, NCS^-, OH^-, NO_3^-, Cl^-, $CO_3^=$, Br^-. We may, therefore, be able to discuss chemical properties of chromic complexes by dint of the spectrochemical series of cobaltic complexes, which have been far more thoroughly investigated than the former.

(4) Applications of the Spectrochemical Series in Preparation. Some of the chemical reactions used in preparing chromic complexes may be easily explained by the spectrochemical series. For example, Christensen's method[11] of preparing $[Cr(NH_3)_6]Cl_3$ and $[Cr(NH_3)_5Cl]Cl_2$ may be mentioned, in which anhydrous chromic chloride is simply kept in contact with liquid ammonia. Anhydrous chromic chloride may be regarded as a polynuclear complex compound, in which chromium atoms are surrounded by six chlorine atoms octahedrally just as in other chromic complexes. Then the rule[5] for substitutions in complex radicals may be applied to this compound: viz., the chlorine ions in complexes can be easily displaced by ammonia molecules, as Cl^- is far behind NH_3 in the spectrochemical series. The substitution takes place so readily that it proceeds rapidly even at the temperatures of liquid ammonia. Anhydrous chromic chloride when it is freshly prepared is almost entirely converted into the luteo-salt. The method of Christensen is, therefore, highly recommended for preparation of the luteo-salt, but it is rather inconvenient for preparing the purpureo-salt, especially when chromic chloride is too fresh. In short, the substitution of NH_3 for Cl^- in liquid ammonia is too rapid for preparing the purpureo-salt. Another method of preparing $[Cr(NH_3)_5Cl]Cl_2$ is based on the same principle. As NH_3 is ahead of H_2O in the series, $[Cr(H_2O)_6](NO_3)_3$ should be converted into $[Cr(NH_3)_6](NO_3)_3$ in liquid ammonia. It is evident from the positions of the ligands in the series that the substitution of NH_3 for H_2O is more difficult than for Cl^-: the latter is too rapid and the former is rather too slow for preparing $[Cr(NH_3)_5Cl]Cl_2$. The present authors, therefore, raised the temperature of liquid ammonia to about 50°C. in order to facilitate the dissociation of $Co–OH_2$ bonds.

Summary.

(1) Absorption spectra of several chromic complexes were measured and it was found that the spectrochemical series is coincident with that for cobaltic complexes.

(2) From the spectrochemical series was discussed the stability of the chromic complexes and some of the methods of preparation were explained.

(3) All the chromic complexes have the first and the second bands. $[Cr(NH_3)_5NCS](NCS)_2$ has another band in addition, which is due to the group $M\leftarrow N{=}C$ (M= a metal-ion of any kind and valency). $[Cr(NH_3)_2(NCS)_4]NH_4$ and $[Cr(NCS)_6]K_3$ have four bands each, the first, the second, the special and the third. The special bands are due to

the same origin as that of $[Cr(NH_3)_5NCS]X_2$ and the third bands are attributed to trans-pairing of the anions.

(4) Chromate ion, a quadri-coördinate complex, has not the first band, but the second and the third, as could be expected from the author's hypotheses.

(5) Absorption spectra of polynuclear compounds may be analysed into those of component complex radicals. For example $[Co(NH_3)_5CrO_4]Cl$ has three bands, of which one is the first band of the sexa-coördinate cobaltic complex and the other two are mainly the second and the third band of quadri-coördinate chromate radical. The second band of the former is almost entirely covered by the second band of the latter.

The authors wish to express sincere thanks to Prof. Y. Shibata for his kind encouragement. They are also indebted to Mr. M. Yanagi for his experimental assistance.

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Synthesis of 3,4-Methylenedioxyphenyl-glyoxal.*

By Sin'iti KAWAI and Koichi ASHINO.

(Received June 23, 1938.)

It is anticipated that the compound in the title will be obtained in yellow crystals or oil. Contrary to our expectation, when homopiperonal (I)[1] was oxidized with selenium dioxide in an alcoholic solution, colourless crystals with m.p. 107° were obtained. Further research upon the colourless compound revealed that it was nothing but the 3,4-methylenedioxyphenyl-glyoxal with one molecule of ethanol of crystallization (III). When the colourless compound was warmed with a boiling ethanol bath in Abderhalden's apparatus under reduced pressure (12 mm.) there remained a yellow oil (II).[2] This yellow oil regenerated the colourless crystals (III) when treated with ethanol.

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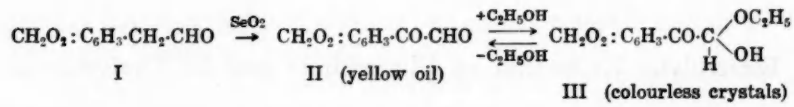
* The same contents will soon be published in Japanese in *J. Chem. Soc. Japan*, **59** (1938), No. 8.

(1) Prepared by the ozonolysis of safrol. Compare S. Nagai, *J. Faculty Eng., Tokyo Imp. Univ.*, **13** (1923), 189.

(2) Since a part of the yellow oil (II) volatilizes with the ethanol of crystallization, the exact content of the latter can not be estimated with this apparatus.



I II (yellow oil) III (colourless crystals)

The disappearance of the yellow colour, the sign of α-diketones, in compound III can probably be attributed to the transformation of one of the carbonyl groups into the hemi-acetal form.

When compound III was treated with more than two molecules of phenylhydrazine, it gave the corresponding mono-phenylhydrazone. *o*-Phenylene-diamine, when mixed with compound III, produced the corresponding quinoxaline-derivative.

Experimental.

Molecular Compound between 3,4-Methylenedioxyphenyl-glyoxal and Ethanol (III). An alcoholic solution of homopiperonal (3.3 g.) and selenium dioxide (4 g.) was refluxed on a steam-bath for two hours. After cooling the selenium which precipitated in the meanwhile was filtered off and the filtrate was concentrated to a small bulk. The colourless crystals mingled with selenium which appeared in the meantime was collected and recrystallized from ether. Colourless long prisms, m.p. 107°. Yield 1 g. Found[3]: C, 58.30, 58.30; H, 5.62, 5.67. Calculated for $C_{11}H_{12}O_5$ (III): C, 58.48; H, 5.35%.) Fuchsine-sulphurous acid reaction was positive.

3,4-Methylenedioxyphenyl-glyoxal-mono-phenylhydrazone. Compound III (1 g.) and phenylhydrazine base (1.2 g.) were dissolved in glacial acetic acid which had been diluted with a little amount of water. Soon the mono-phenylhydrazone crystallized out, which was collected and recrystallized from ethyl alcohol, orange-yellow prisms, m.p. 140°. Yield 0.4 g. Found: N, 10.07. Calculated for $C_{15}H_{12}O_3$: N, 10.44%.

2-[3′, 4′-Methylenedioxyphenyl]-quinoxaline. Compound III (0.1 g.) and *o*-phenylene-diamine (0.6 g.) were dissolved in a small quantity of ethyl alcohol with gentle warming and then cooled. Soon the crystals of the quinoxaline derivative made their appearance, which were collected and recrystallized from ethyl alcohol, slightly yellow prisms, m.p. 167.5°. Yield 0.1 g. Found: C, 71.56; H, 4.07; N, 11.09. Calculated for $C_{15}H_{10}O_2N_2$: C, 71.99; H, 4.03; N, 11.20%.

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Tokyo-Bunrika University.

(3) The microanalyses of this compound according to Pregl's method, prosecuted by Kisaburo Yamagami, were successful only when they were carried out first in nitrogen stream and then in oxygen. The ordinary method gave a little too small values of carbon and hydrogen since the ethanol of crystallization burned suddenly at the commencement of the analyses.

Electrolytic Reduction of Glutarimide and Its Derivatives.

By Buhei SAKURAI.

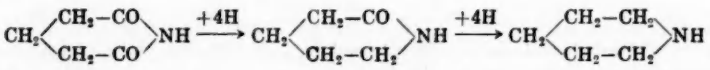
(Received June 25, 1938.)

As a rule reduction of acid imides is very difficult; complete reduction of even one of two carbonyl groups is often found unattainable by purely chemical means, that of both carbonyls being almost impossible. Electrolytically, however, reduction takes place with much ease, and by controlling the conditions of reduction properly it is not difficult to prepare the reduction product in some desired stage.

The results of electrolytic reduction of succinic acid imide,[1] undertaken by the author were previously communicated. The work was now extended to next higher dibasic acid imide, i.e. glutarimide, and the result so far obtained is here reported.

So far as the author could find in chemical literature, no one seems to have yet succeeded in getting piperidone or piperidine and their derivatives by direct reduction of glutarimide and its derivatives. Wallach[2] and L. Ruzicka[3] tried to reduce *N*-ethyl-piperidone with metallic sodium in alcoholic solution, and obtained a condensation product consisting of two molecules of piperidone but not *N*-ethyl-piperidine.

When electrolytically reduced, glutarimide and its derivatives change into piperidines passing through the stage of piperidones:



The first reduction takes place smoothly when lead is used as cathode in sulphuric acid solution. For the second reduction lead cathode prepared with a special care according to Lukes and Smetachova[4] should be used. The author found out that zinc amalgam is much more effective for the same purpose.

Of *N*-methyl-, *N*-ethyl-, and *N*-phenyl-glutarimides, the first two could be reduced easily and with comparatively little decomposition in an about 50% sulphuric acid solution, with lead cathode to *N*-methyl- and

(1) B. Sakurai, this Bulletin, **10** (1935), 311; **11** (1936), 41; **13** (1938), 350.
(2) Wallach, *Ann.*, **324** (1902), 285.
(3) L. Ruzicka, *Helv. Chim. Acta*, **4** (1921), 472.
(4) Lukes and Smetachova, *Collection Czechoslov. Chem. Commun.*, **5** (1933), 61.

N-ethyl-piperidones, respectively, and with zinc amalgam cathode to *N*-methyl- and *N*-ethyl-piperidines.

Glutarimide and *N*-phenyl-glutarimide are much more liable to decompose in the same sulphuric acid catholyte. So that, if careful attention be not paid to the concentration of sulphuric acid, fruitless results are obtained. It is to be noted that the concentrations of sulphuric acid which cause decomposition of glutarimide and *N*-phenyl-glutarimide differ widely from each other. In the case of glutarimide the most suitable concentration of sulphuric acid is 20–30%. If more concentrated, glutarimide begins to be decomposed to glutaric acid and ammonia and finally in the solution containing H_2SO_4 more than 70% complete decomposition takes place giving no reduction product. In the case of *N*-phenyl-glutarimide the solution containing 80–90% H_2SO_4 is found the most favourable for reduction. If H_2SO_4 becomes less concentrated than 60%, phenyl-glutarimide completely decomposes into glutaric acid and aniline, yielding no reduction product. Reduction from piperidone to piperidine does not differ in both cases, smooth reduction taking place in an about 50% acid solution. The degree of decomposition also differs according to the kind of cathode, and as zinc amalgam causes less decomposition than lead, it is preferable to use a 50% sulphuric acid solution from the beginning in the case of glutarimide, and to increase the concentration of sulphuric acid in electrolytic solution by adding concentrated sulphuric acid to it after the first reduction has been completed. As it is impossible to employ 50% acid and zinc amalgam cathode for *N*-phenyl-glutarimide, a 90% acid solution is to be used with lead cathode for the first reduction, and then the electrolytic solution is diluted to make H_2SO_4 50% and at the same time lead cathode is replaced with zinc amalgam before electrolysis is continued for the second reduction.

Experimental.

I. **Glutarimide,** $CH_2\langle^{CH_2-CO}_{CH_2-CO}\rangle NH$. Material was prepared after Bernheimer by fusing ammonium glutarate, and by recrystallizing the residue from alcohol. This forms colourless plates melting at 151°.

(1) *Reduction with lead cathode.* In order to obtain α-piperidone, electrolysis was undertaken under the following conditions. Cathode: lead, 100 sq. cm. Catholyte: 25% sulphuric acid with 3 g. of the imide dissolved in it. Current density: 5 amp. per 100 sq. cm. Current quantity: 7.2 F. per mol. Temperature: 20°.

The electrolytic bath was kept in a water tub full of cool water, and electrolyte was kept all the time stirred and cooled. After electrolysis colourless electrolyte was taken out, and treated with chloroform to extract unreduced material. Next

it was shaken with ether to extract glutaric acid produced through the decomposition of the material. After that the liquid was made alkaline with a saturated solution of sodium carbonate, when smell peculiar to α-piperidone came out. It was extracted with ether, and after expelling ether by evaporation about 3 c.c. of a liquid solution were obtained. It was put in a desiccator and then cooled in an ice-box, whereupon 0.4 g. (15%) of α-piperidone crystallized out. On recrystallizing it from ether colourless crystals melting at 38° were obtained. The platinum double chloride was obtained in yellow plates soluble in water or alcohol and melting at 176° with decomposition. Found: Pt, 32.05. Calculated for $\left[CH_2\begin{matrix}CH_2-CO\\CH_2-CH_2\end{matrix}NH\right]_2+H_2PtCl_6$: Pt, 32.07%.

From the above result, it is seen that, though the imide may be reduced to α piperidone, its greater part decomposes into glutaric acid and ammonia in the course of electrolysis.

To see how the decomposition of glutarimide is related to concentration of sulphuric acid a series of experiments were carried out varying concentration of sulphuric acid. The results were summarised in Table 1.

Table 1.

Conc. of sulphuric acid (%)	Unchanged material (%)	Glutaric acid (%)	α-Piperidone (%)
20	10	34	11
30	7.5	43	14
40	5.0	47	11
50	5.0	47	8.6
60	2.5	51	5.7
70	1.0	51	2.8
80	—	55	—
90	—	64	—

As is seen from the table, sulphuric acid of 20–30% seems to be most favourable for the production of α-piperidone.

(2) *Reduction with zinc amalgam cathode.* With the object of getting piperidine electrolysis was conducted using zinc amalgam as cathode under the following conditions. Cathode: zinc amalgam, 15.8 sq. cm. in area. Catholyte: 50% sulphuric acid 100 c.c. with 5 g. of imide dissolved in it. Anode: cylindrical plate of lead. Anolyte: 50% sulphuric acid. Current density: 88.6 amp. per 100 sq. cm. Current quantity: 70.8 F. per mol. Temperature: 25°.

Into the catholyte a spiral lead tube was inserted, through which cold water was passed, while the electrolytic bath itself was put in a water tub full of cool water to prevent the temperature from rising. The catholyte was kept stirred all the time. After electrolysis no glutarimide was detected in the catholyte, but about 0.5 g. (8.5%) of glutaric acid was isolated from it. When it was made alkaline by adding a saturated solution of sodium carbonate, there came out a strong smell re-

sembling that of ammonia. The alkaline solution was extracted with ether, and on the evaporation of ether about 3 c.c. of an aqueous liquid were obtained as the residue. This was made acidic by adding hydrochloric acid to it and evaporated to dryness on the water bath when 2.5 g. (47%) of piperidine hydrochloride was produced. Its platinum double chloride formed orange-red crystals easily soluble in water and alcohol, and melting at 198° with decomposition. Found: Pt, 33.60. Calculated for $\left[CH_2\langle^{CH_2-CH_2}_{CH_2-CH_2}\rangle NH\right]_2 + H_2PtCl_6$: Pt, 33.62%.

The particularly noteworthy fact observed is that the decomposition of the material is less with zinc amalgam cathode than with lead cathode, in the solution containing sulphuric acid of the same concentration.

II. **α-Piperidone,** $CH_2\langle^{CH_2-CO}_{CH_2-CH_2}\rangle NH$. 1.5 g. of the piperidone obtained in the above experiment was subjected to 5 hours' electrolysis with zinc amalgam under the same conditions as above. As the result, 0.95 g. (52%) of piperidine hydrochloride was obtained, accompanied with a very little decomposition product. It is thus seen that piperidone is not so decomposable as glutarimide in sulphuric acid solution. The reason why the cathode of stronger reducing power, such as zinc amalgam, gives the better yield of reduction product is thus easily understood.

III. **N-Ethyl-glutarimide,** $CH_2\langle^{CH_2-CO}_{CH_2-CO}\rangle NC_2H_5$. *N*-Ethyl-glutarimide employed in the experiment was prepared by neutralizing glutaric acid with ethylamine and then subjecting the product to distillation at 250–260°. It is a colourless liquid.

(1) *Reduction with lead cathode.* To get *N*-ethyl-piperidone first, electrolysis, was undertaken under the following conditions. Cathode: lead plate 100 sq. cm. in area. Catholyte: 100 c.c. of 50% sulphuric acid in which 5 g. of imide was dissolved. Anode: cylindrical lead plate. Anolyte: 50% sulphuric acid. Current density: 5 amp. per 100 sq. cm. Current quantity: 26.3 F. per mol. Temperature: 28°.

The material dissolved readily in electrolytic solution. The electrolytic bath was kept cooled in a water tub in which cool water was caused to circulate. After the completion of the electrolysis the electrolytic solution was shaken with ether to extract glutaric acid. About 0.25 g. (5%) of it was obtained. Next, after greater part of acid was neutralized with sodium bicarbonate, the catholyte was made slightly alkaline with a saturated solution of sodium carbonate and then extracted with ether when 3.25 g. of a colourless liquid was isolated. It boils at 105–106°, and is easily soluble in water forming a weakly alkaline solution. Its platinum double chloride melts at 164° with decomposition. Found: Pt, 29.39. Calculated for $\left[CH_2\langle^{CH_2-CO}_{CH_2-CH_2}\rangle NC_2H_5\right]_2 + H_2PtCl_6$: Pt, 29.40%. Yield of *N*-ethyl-piperidine in the above experiment is 72.1%.

In the reduction of *N*-ethyl-glutarimide, the concentration of sulphuric acid has close relation to the yield of reduction product; the greater the concentration, the smoother the reduction. If, however, the concentration becomes too great, it gives rise to the decomposition of the material, thereby lowering reduction rate.

Results of the electrolysis showing the relation between the concentration of sulphuric acid and yield of the piperidone are shown in Table 2.

Table 2.

Conc. of H_2SO_4 (%)	Glutaric acid (%)	*N*-Ethyl-piperidone (%)
20	5.4	5.5
30	6.5	44.0
40	7.6	55.0
50	10.8	71.5
60	11.9	77.0
70	16.2	60.5
80	43.2	27.5
90	59.4	5.5

From the table it is seen that if the concentration of sulphuric acid exceeds 70%, decomposition increases rapidly, causing the lowering of reduction rate, and 40–70% sulphuric acid gives the most favourable results.

(2) *Reduction with zinc amalgam cathode.* Next electrolysis for complete reduction was conducted under the following conditions. Cathode: zinc amalgam 15.8 sq. cm. Catholyte: 100 c.c. of 50% sulphuric acid in which 5 g. of imide was dissolved. Anode: cylindrical lead plate. Anolyte: 50% sulphuric acid. Current density: 98 amp. per 100 sq. cm. Current quantity: 126 F. per mol. Temperature: 15°.

The electrolysis was carried out by inserting a spiral lead tube into a cylindrical biscuit vessel containing catholyte. Cold water was caused to flow through the lead tube to cool it from inside, while the electrolytic bath itself was put in a water tub, in which cold water constantly circulates to cool the bath from outside. After completion of electrolysis neither the glutarimide nor glutaric acid was detected to exist in the bath. The electrolyte was now diluted with water of three times volume and after neutralizing the acid with sodium bicarbonate it was made slightly alkaline with a saturated solution of sodium carbonate. It was then subjected to steam distillation, when a substance smelling like ammonia came out. The distillate reacting alkaline to litmus paper was neutralized with hydrochloric acid and evaporated to dryness on the water bath. About 4.0 g. of a sticky substance was left as the residue. The platinum double chloride prepared from the residue crystallized in orange-red prisms from a mixture of absolute alcohol and a small quantity of petroleum ether. It melted at 202° with decomposition. Found: Pt, 30.74. Calculated for $\left[CH_2\begin{matrix}CH_2-CH_2\\ CH_2-CH_2\end{matrix}NC_2H_5\right]_2+H_2PtCl_6$: Pt, 30.70%. The yield of *N*-ethyl-piperidine amounted to 75%.

IV. ***N*-Ethyl-piperidone**, $CH_2\begin{matrix}CH_2-CO\\ CH_2-CH_2\end{matrix}NC_2H_5$. Instead of directly reducing *N*-ethyl-glutarimide, 2 g. of *N*-ethyl-piperidone was subjected to 5 hours' electrolysis under exactly the same conditions as the above experiment. As the result *N*-ethyl-piperidine was obtained with the yield of 52%.

V. **N-Phenyl-glutarimide,** $CH_2\begin{matrix}CH_2-CO\\CH_2-CO\end{matrix}NC_6H_5$. *N*-Phenyl-glutarimide was prepared from glutaric acid and aniline and purified by recrystallizing the product from absolute alcohol. It formed colourless needles insoluble in water but easily soluble in hot alcohol, and melted at 145°.

(1) *Reduction with lead cathode.* With a view to obtaining *N*-phenyl-piperidone, hitherto unknown, reduction was carried out under the following conditions. Cathode: lead plate 100 sq. cm. Catholyte: 100 c.c. of 90% sulphuric acid in which 5 g. of imide was dissolved. Anode: cylindrical lead. Anolyte: 50% sulphuric acid. Current density: 5 amp. per 100 sq. cm. Current quantity: 56.4 F. per mol. (8 hours). Temperature: 18°.

Electrolysis was carried out by cooling the electrolytic bath with circulating water and keeping catholyte constantly vigorously stirred. The imide partly remained undissolved at first, but gradually disappeared as electrolysis proceeded. After electrolysis the catholyte was diluted with three times as much water and filtered. The clear solution thus obtained was found to contain nothing to be extracted with ether. It was then made slightly alkaline with sodium bicarbonate and sodium carbonate, and from this alkaline solution about 3.5 g. (75%) of *N*-phenyl-piperidone was extracted in the form of brownish crystals. When it was recrystallized from alcohol it formed colourless needles melting at 98°. Found: C, 75.10; H, 7.47; N (determined as ammonia), 8.04%; mol. wt. (ebullioscopy in benzene), 170. Calc. for $C_{11}H_{13}ON$: C, 75.43; H, 7.43; N, 8.00%; mol. wt., 175. The platinum double chloride of this substance formed red-brown scaly crystals melting at 176° with decomposition. Found: Pt, 25.65. Calculated for $\left[CH_2\begin{matrix}CH_2-CO\\CH_2-CH_2\end{matrix}NC_6H_5\right]_2+H_2PtCl_6$: Pt, 25.69%.

As is obvious from the results of above experiment, the reduction of phenyl derivatives greatly differs from that of ethyl derivatives. For reduction of the former much more concentrated sulphuric acid solution is required. If more dilute sulphuric acid be used as in the reduction experiment for other imide derivatives, decomposition predominates over reduction, making reduction efficiency very bad. The relation existing between concentration of sulphuric acid and the yield of piperidone formed by reduction is shown in Table 3.

Table 3.

Conc. of sulphuric acid (%)	Unchanged material (%)	Glutaric acid (%)	*N*-Phenyl-piperidone (%)
90	—	—	76
80	10	—	54
70	—	48	36
60	20	58	—
50	25	64	—

Thus, high concentration of sulphuric acid favours the reduction. When concentration of sulphuric acid gets below 60% any reduction is effected no more. In

order to reduce *N*-phenyl-glutarimide without any loss in material it is necessary to maintain the concentration of sulphuric acid at a value not smaller than 80%.

(2) *Reduction with zinc amalgam cathode.* In the experiment conducted with the object of obtaining the final reduction product, *N*-phenyl-piperidine, it is inconvenient to work with zinc amalgam cathode in a concentrated sulphuric acid bath. Because not only it checks the passage of electricity, but also it causes decomposition of sulphuric acid. So that, it is advisable to divide the experiment into two stages. In the first stage electrolysis is carried out, as with lead cathode, in 90% sulphuric acid solution to reduce the imide to the piperidone stage and then the electrolytic solution is diluted to make concentration of H_2SO_4 as low as 50% and further electrolysis is carried out with zinc amalgam.

The first stage of reduction carried out with 5 g. of imide was followed by the second stage of reduction, for which the following conditions were employed. Catholyte: 100 c.c. of 90% sulphuric acid which was diluted with 130 c.c. of water. Cathode: zinc amalgam, 15.8 sq. cm. in area. Anolyte: 50% sulphuric acid. Anode: cylindrical lead plate. Current density: 79 amp. per 100 sq. cm. Current quantity: 101.5 F. per mol. (6 hours). Temperature: 18°.

In the course of electrolysis, the electrolytic solution was cooled from both inside and outside. After electrolysis the catholyte contained some sulphur isolated by the decomposition of sulphuric acid. It was filtered and the filtrate was made alkaline with sodium bicarbonate and sodium carbonate solution, when oily *N*-phenyl-piperidine was isolated, which was extracted with ether. About 2.5 g. of the base (58% yield) was obtained. *N*-Phenyl-piperidine is a colourless oil, soluble in water, and easily produces a colourless soluble salt with hydrochloric acid. Its platinum double chloride is yellow crystals containing two molecules of water of crystallization, insoluble in water. It melts with decomposition. Found: Pt, 25.45. Calculated for $\left[CH_2\begin{matrix}CH_2-CH_2\\CH_2-CH_2\end{matrix}NC_6H_5\right]_2+H_2PtCl_6\cdot 2H_2O$: Pt, 25.42%.

In this connection the author expresses his heartfelt thanks to Dr. Motooki Matsui, Professor emeritus of the Kyoto Imperial University, for his cordial suggestions.

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Sumiyoshi, Osaka.

On the Silver Chromate Banding in Silicic Acid Gel.

By Toshizo ISEMURA.

(Received June 15, 1938.)

It was stated that silver chromate readily forms periodic banding in gelatine, but not in agar-agar or in silicic acid. But by suitably modifying the conditions, Bradford[1] could obtain the bands of silver chromate in agar-agar. On the other hand, Dhar and Chatteriji[2] concluded that the banding was formed by periodic coagulation of peptised sol. The silicic acid has not the peptising power on silver chromate, so that silver chromate does not form bands in silicic acid gel. This case is frequently pointed out as an example of the specific influence of the gel as a medium for the reaction. On the contrary to Dhar and Chatteriji's presentation, Hatschek[3] has succeeded in obtaining the bands of silver chromate in silicic acid gel. He had prepared the gel by an unusual method, based on the fact that the silicic acid is gelatinised on mixing a sodium silicate solution with a somewhat large quantity of potassium dichromate solution. After setting the gel he superposed a concentrated solution of silver nitrate on it. He could thus obtain the banding of silver chromate in silicic acid gel.

When we persuit the experiments of rhythmic precipitates in silicic acid gel, usually the gel is prepared as follows. One volume of sodium silicate solution is mixed with an equal volume of solution of some acid, pouring the water glass into the acid and mixing quickly and thoroughly, and then the inner electrolyte is added into it to adequate concentration. After setting the gel, diffusing electrolyte is superposed on it. The present author tried to make the silver chromate bands in the silicic acid gel which was made by this usual procedure. It was recognised with many experiments on the formation of rhythmic banding in silicic acid gel, that the concentration of the acid which is used to make a gel, that is to say, the hydrogen ion concentration of the gel, has a profound influence on whether the bands are formed or not. The fact that the formation of the rhythmic bands of silver chromate had been hitherto unobtainable seemed to be owing to the hydrogen ion concentration of the silicic acid

(1) Bradford, "Alexander's Colloid Chemistry, Theoretical and Applied," Vol. I, 790, New York (1926).

(2) Dhar and Chatteriji, *Kolloid-Z.*, **37** (1925), 89.

(3) Hatschek, *ibid.*, **38** (1926), 151.

gel. In the present study, the silicic acid gels were made by mixing equal volumes of sodium silicate solution (density 1.06) and nitric acid solutions having different concentration. The obtained results in these gels are summarised in the following table.

Table 1. $AgNO_3$ 5%; 6.0 c.c. of Na_2SiO_3 (1.06) solution + 6.0 c.c. of HNO_3 + 0.4 c.c. of 5% $K_2Cr_2O_7$.

Concentration of HNO_3 N)	Nature of the rhythmic banding
0.67	Typical rhythmic precitates consisting of relatively coarse crystals of red black plates were obtained. The intervals between bands were large.
0.63	Typical rhythmic precipitates as shown in Fig. 1. (the left of the three) were obtained. Crystals were small needles.
0.58	At the top of the gel Liesegang bands accompanied by dendrites were recognised. In the middle, only dendrites were seen, and at the bottom again rhythmic bands appeared but they were those formed by diurnal cause.
0.55	The result was analogous to the case of 0.58 N. But the number of formed Liesegang bands was less.
0.50	No Liesegang band was formed. Dendrites and diurnal bands were seen.

With more concentrated nitric acid than 0.70 N, the silicic acid is not gelatinised. From the foregoing table we can recognise that in the gel of relatively high hydrogen ion concentration the silver chromate banding is formed. In the gel of low hydrogen ion concentration, the decomposition of sodium silicate is not complete, and the rest of sodium silicate reacts with silver nitrate, and so silver silicate is also formed. The silver chromate forms with this silver silicate either complicated bands accompanied by dendrites or only dendrites. The colour of the precipitates forming well-defined bands is red-black but the colour of dendritic bands or dendrites is reddish brown. As frequently stated in older literatures, the banding could not obtained in silicic acid gel, because of the comparatively narrow range of the acidity that is favourable to the band formation of silver chromate.

According to Hatschek's method, somewhat large quantity of potassium dichromate is needed, for it must gelatinise the silicic acid gel. As

the result of the existence of a large quantity of potassium dichromate, the obtained bands are close to each other and the empty spaces between the bands blurred and hardly discriminated. By the method which is now presented, we can regulate the concentration of potassium dichromate at will. The formed bands are more distinct being marked by gaps and empty spaces.

The influence of the kinds of acids which are used to make the gel, was also investigated. Of course, hydrochloric acid is inadequate for this purpose, because it unites with silver nitrate and precipitates an almost completely insoluble silver chloride. So, nitric, sulphuric and acetic acids were used.

Nitric acid is the most favourable, sulphuric acid comes next. Acetic acid forms silver acetate, that is somewhat difficultly soluble. And in the gel which is made by mixing sodium silicate solution and acetic acid, crystals of silver acetate grow in long needles. In the gel which is made from sodium silicate and sulphuric acid, silver sulphate crystals are also formed at the top of the gel, but this is not so remarkable as in the case of acetate. Fig. 1 shows the silver chromate banding in silicic acid gels. From left, the gels were made by mixing sodium silicate solution with nitric, sulphuric, and acetic acid respectively. Crystals formed in these gels are variously shaped. In many cases they are needles. At the bottom of a test-tube, the needle measures often more than 8 mm. long. But they are sometimes plates. These crystals were compared under a microscope, and observed that they consist of many small crystals. The needles were fern-like fronds under a microscope.

The plates are as shown in Fig. 2. The appearances of each crystals were rather different, but a single crystal separated from either a needle or a plate was the same. It crystallises in elongated hexagonal plates. Single crystals are taken in photograph and shown in Fig. 3.

As Hatschek[3] has already pointed out, Dhar and Chatteriji's coagulation theory[4] about the formation of rhythmic precipitates is not applicable. They support their theory with the non-formation of silver chromate bands in silicic acid.[2] But the last mentioned fact is clearly denied by the present experiments. Also the membrane theory is not correct, because the crystals in banding are separated from each other, no membrane formation being recognisable in the rhythmic precipitates, what may be observed in the photograph. The bands consist of well-

(4) Dahr and Chatteriji, *Kolloid-Z.*, **31** (1922), 15; **37** (1925), 2; **37** (1925), 89.

(5) Fischer and McLaughlin, *ibid.*, **30** (1922), 13; Traube and Takehara, *ibid.*, **35** (1924), 245.

developed crystals separated by relatively large spaces, allowing free passage to the diffusing electrolyte.

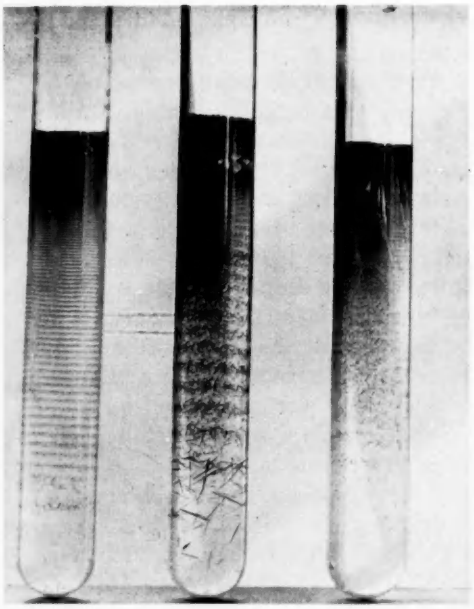
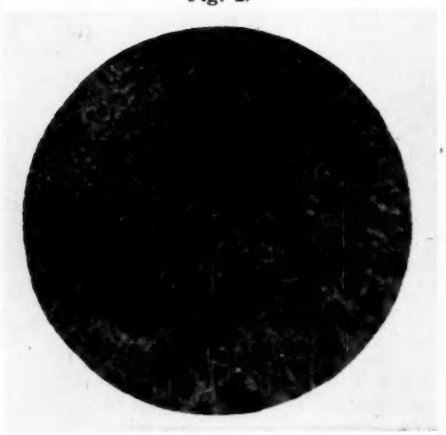


Fig. 1.

(×95)

Fig. 2.



(×310)

Fig. 3.

Summary.

(1) The formation of silver chromate bands in silicic acid gel which was made by a usual method, has been described.

(2) By this procedure, the concentration of chromate is regulated at will, and distinct banding is formed.

(3) The hydrogen ion concentration of the gel has a profound influence on the formation of rhythmic bands of silver chromate.

(4) Dhar and Chatteriji's theory and the membrane theory are not applicable.

In conclusion the author wishes to express his cordial thanks to Prof. J. Sameshima of the Tokyo Imperial University for his kind advices.

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On the Calcium Phosphate Banding in Silicic Acid Gel.

By Toshizo ISEMURA.

(Received June 27, 1938.)

In regard to the formation of rhythmic precipitate of calcium phosphate in other medium than a silicic acid gel, several reports have been published. There have been the studies of Dogadkin,[1] Hatschek,[2] and Schemjakin[3] concerning the formation in a gelatine gel and those of Schemjakin on the phenomenon in an agar-agar gel. As to the rhythmic precipitation of this substance in a space between two pieces of glass and in capillary spaces without the aid of any gels, the studies of Doyle and Ryan[4] and Wo. Ostwald[5] can be mentioned. But the banding in a silicic acid gel have never been reported. Therefore, the present author has tried an experiment in order to know whether the Liesegang phenomenon of calcium phosphate could be caused or not in the silicic acid gel. And it was certified that calcium phosphate produced an extremely prominent rhythmic precipitate even in a silicic acid gel and that the banding

(1) *Kolloid-Z.*, **40** (1926), 33.
(2) *Kolloid-Z.*, **27** (1920), 225; *Biochem. J.*, **14** (1920), 418.
(3) *Kolloid-Z.*, **50** (1930), 58.
(4) *Brit Chem. Abstract*, A, **1929**, 1144; *Proc. Roy. Irish Acad.*, B, **38** (1929), 435.
(5) *Kolloid-Z.*, **40** (1926), 144.

was closely related to the hydrogen ion concentration of the medium or a silicic acid gel. The experimental result will be described in the following.

Although calcium salts were used as an inner electrolyte and sodium phosphate made diffuse into the gel in all the cases hitherto reported, whichever the inner electrolyte might be, calcium salts or sodium phosphate, as favourable a result was obtained in a silicic acid gel as in other gels. There was a marked difference between the silicic acid and other gels. Use of sodium phosphate as an inner electrolyte had rather a strong point that preparation of gel needed no special care. In use of calcium salts as an inner electrolyte, acetic acid, sodium silicate and calcium salt should be mixed in the order and the mixture stirred up rapidly. Unless these were mixed in this order or unless the mixture stirred up rapidly, white turbidities, which seemed to calcium silicate, were formed, partially coagulated, so that no transparent gel could be obtained. Use of sodium phosphate and the likes as an inner electrolyte, on the contrary, needed no special care. But in either case where a phosphate solution was added to diffuse into the gel containing a calcium salt or where a calcium salt solution was poured on the gel containing a phosphate, a rhythmic precipitate with very clear bands was obtained.

The following can be mentioned as one of the most favourable conditions. That is, for dissolving phosphate in a gel, mix 1 c.c. of a 8% solution of secondary sodium phosphate with 10 c.c. of a 0.75 N acetic acid and then add 10 c.c. of a 1.06 density solution of sodium silicate to it and allowed to stand to gelatinize. After the gel set firmly, a 2 mol solution of calcium nitrate was superimposed on it.

For dissolving calcium salt in a gel, after mixing the sodium silicate solution ($d = 1.06$) with 10 c.c. of 0.75 N acetic acid add 1.0 c.c. of a 10% calcium chloride solution to the mixture, while stirring up. After the gel set firmly, a 8% solution of secondary sodium phosphate was poured on it.

The right of Fig. 1 shows the bands formed by the former method and the left, those obtained by the latter method. Fig. 2 shows Liesegang rings of calcium phosphate formed on a glass plate by the former method.

The effect of the hydrogen ion concentration, inner electrolyte and its concentration, outer electrolyte and its concentration, concentration of gel, and, moreover, the effect of aging on the formation of this rhythmic precipitate have been examined, and the results are described in the following lines.

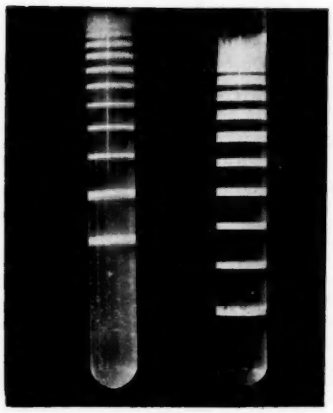

Fig. 1.

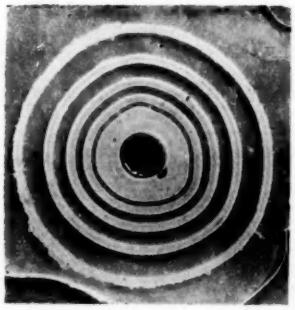

Fig. 2.

Effect of Hydrogen Ion Concentration. It has already been mentioned that the hydrogen ion concentration has a very marked effect on the formation of these bands. At first, the case where calcium chloride was used as the inner electrolyte will be described. If the hydrogen ion concentration was low in the addition of calcium chloride to a silicic acid sol, a partial coagulation occurred and produced a curdy precipitate; accordingly it was impossible to prepare a uniform gel. This is probably caused by the fact that the calcium salt was acted simultaneously by an amount of sodium silicate, which remained undecomposed, in the process of the formation of silicic acid by the action of acid, which was small in quantity.

In employment of a sol containing a little more concentrated acid, for instance, a sol which was prepared by mixing 0.66 N acetic acid and an equal volume of sodium silicate solution of 1.06 density, an uniform gel could be obtained. By diffusion of sodium phosphate into the gel, however, a long zone of white precipitate was formed, which was not rhythmic.

In a case where an acid was more concentrated, that is, in a case where a gel made from 0.75 N acetic acid and an equal volume of sodium silicate ($d = 1.06$) was used, the rhythmic precipitate could be formed. When the concentration was further more increased, the bands were hardly formed. In a gel composed of 1 N acetic acid and an equal volume of sodium silicate ($d = 1.06$), two or three incomplete bands were only formed on the contact surface of the diffusing solution and the gel.

In short, the formation of rhythmic bands was only possible in the gels which were made from 0.7–1 N acetic acid and an equal volume of a sodium silicate solution ($d = 1.06$). Especially 0.75–0.8 N acetic acid gave a favourable result. This can be seen in Table 1.

Table 1. Na_2SiO_3 ($d = 1.06$); $CaCl_2$ 0.08%; Na_2HPO_4 0.5 mol.

Conc. of acetic acid added (N)	Number of bands formed	Remarks
0.50		
0.66		A continuous zone of precipitate.
0.70	3	After a continuous precipitate as long as 4 cm., extremely thick bands were formed.
0.75	10	Typical rhythmic precipitate.
0.80	13	Typical rhythmic precipitate.
0.90	(15)	The bands were fragmental and incomplete but stood close.
1.00	(3)	Fragmental.

Equal volumes of Na_2SiO_3 and acetic acid were mixed. This result is in the case where the gel was filled to a height of 8 cm. of a test-tube of 1 cm. in internal diameter and 14 cm. in length.

The results were the same, where secondary sodium phosphate was used as the inner electrolyte. When a sodium silicate solution ($d = 1.06$) was mixed with an equal volume of 0.5, 0.6, and 0.7 N acetic acid respectively, the uniform gel could generally be obtained. When a calcium salt was allowed to diffuse into them, however, there formed only a zone of completely even white precipitate. When the acid or hydrogen ion is further more concentrated, the rhythmic precipitation may occur. As the concentration of acetic acid increased, the number of formed bands gradually decreased. No band was formed by the used of 2 N acetic acid. The results are given in Table 2.

Calcium phosphate was precipitated as the primary, secondary or tertiary calcium phosphate according to the value of pH of the gel in which the precipitation occurred. Therefore the primary salt can probably form no rhythmic bands on account of its solubility; while the secondary or tertiary salt can produce the rhythmic precipitate. When pH of the gel is high, the tertiary salt only formed, and it precipitates rather unrhythmical because a salt of too poor solubility, gives generally no rhythmic bands. Judging from these facts, the absence of rhythmic precipitate in this case is acknowledged.

Table 2. Na_2SiO_3 ($d = 1.06$); Na_2HPO_4 0.4%; $CaCl_2$ 30%.

Conc. of acetic acid (N)	*p*H	Number of bands formed	Remarks
0.60	8.98		Continuous precipitate formed.
0.70	7.72		,,
0.75	7.04	9	
0.80	6.01	7	
0.90	5.50	4	
1.00	5.30	3	
2.00	4.67	0	No precipitate formed.

The gel was made by mixing the equal volumes of sodium silicate and acetic acid. As much of the gel was taken as to fill to a height of 6 cm. of a test tube of 1.2 cm. in internal diameter and 11 cm. in length.

Inner Electrolyte and the Effect of Its Concentration. As already mentioned, calcium salts as well as sodium phosphate are usable as an inner electrolyte. At first the case of calcium chloride will be described. The experiment was conducted in a gel which was made from 0.75 N acetic acid and sodium silicate solution of 1.06 in density, containing calcium chloride in various composition from 0.004 to 5%.

The rhythmic precipitate was formed in any gels containing calcium chloride in higher concentrations than 0.017%. But when the amount of calcium chloride exceeds 5%, then a 0.5 mol solution of secondary sodium phosphate was hardly diffused into the gel and a stopper of precipitate was only formed on the surface contacting the gel. Yet generally, when calcium chloride was more concentrated, though all the other conditions were the same, the formed bands were large in number and stood close. If the concentration was beyond a certain limit, the bands increased their thickness, but the number of bands rather decreased. This was probably because by the osmotic pressure of the electrolytes in the gel. The diffusion became difficult into such a gel which contained so much inner electrolyte. The results are given in Table 3.

As much of a gel was taken as to fill to a height of 8 cm. of a test-tube of 1 cm. in internal diameter and 0.5 mol secondary sodium phosphate solution was allowed to diffuse in it. When calcium chloride was too much concentrated, the band of calcium phosphate which was formed on the contact surface of the gel and diffusing agent was broken by the osmotic pressure of calcium chloride solution. Then a new precipitate

Table 3. Outer electrolyte: Na_2HPO_4 0.5 mol.

Conc. of inner electrolyte $CaCl_2$ (%)	Number of bands formed	Remarks
5.00	0	Dendrites grew in the diffusing solution.
2.50	2	
1.50	8	The bands formed in the lower part of gel were fragmental.
0.50	9	
0.30	9	
0.15	11	
0.08	10	
0.03	6	
0.017	2	
0.010	0	
0.004	0	

The gel was made by mixing equal volumes of Na_2SiO_3 ($d = 1.06$) and acetic acid (0.75 N). The asterisk in the subsequent tables shows that such a gel was used.

was formed there and it grew in dendrites in the solution of secondary sodium phosphate as the diffusing solution. This seemed to be ascribed to the same cause as that the silicates of cobalt, nickel, and manganese, etc. grew in dendrites in a sodium silicate solution which is known as a "chemical garden" and that the copper ferrocyanide grew in a saccate form in a potassium ferrocyanide solution. An example is given in Fig. 3. It was a matter of course that this could be produced also when a sodium phosphate solution was added slowly to a concentrated solution of calcium chloride, or solid calcium salt.

When gels were prepared in the same conditions, except for employment of sodium phosphate as the inner electrolyte instead of calcium chloride, so far as the experiment is conducted in the range of 0.0125–1.25%, the gels containing the sodium phosphate in higher concentrations than 0.038%, always gave very clear rhythmic precipitates. If the inner electrolyte was small in concentration, the stopper of precipitate which was formed first of all, was large and the distances between the successive bands were large. Contrary to the case where calcium chloride was used as the inner electrolyte, if the inner elektrolyte was small in concentration, each band was rather thick. This was not because the precipitate was separated in abundance, but because the locality of the deposition was sharp in either side, having a certain

width. The relation between the concentration and the number of formed bands is given in Table 4, where each band was as thick as 5 mm. in the case of the least concentrated inner electrolyte.

Fig. 3.

Table 4.* Outer electrolyte: $CaCl_2$ 30%.

Conc. of inner electrolyte Na_2HPO_4 (%)	Number of bands formed
1.25	13
1.08	12
0.87	10
0.54	8
0.13	5
0.07	3
0.038	2
0.0125	0

In experiment with the inner electrolyte of such other salts than secondary sodium phosphate, as primary potassium phosphate or tertiary sodium phosphate, 0.5 c.c. of each 0.5 mol primary or tertiary salt was added to each 10 c.c. of the sol composed of sodium silicate ($d = 1.06$) and an equal volume of 0.75 N acetic acid, in order to obtain a gel. In the gel containing the primary salt, the precipitate was formed rhythmically, while in the gel containing the tertiary salt, a continuous precipitate was obtained. But the rhythmic precipitation was recognised by adding half the quantity of the tertiary salt or by using 0.8 N acetic acid in preparation of the gel.

From the measurement of the *p*H in these cases, the rhythmic precipitation was possible in the gels of lower *p*H values than about 7.6. Therefore, it is not an important factor that which salt should be added, the primary, secondary, or tertiary one but the hydrogen ion concentration of the gel is an essential factor. The formation of the rhythmic precipitate was possible in the case where the *p*H was about 5.3–7.6; that is where the inner electrolyte was a mixture of the primary and secondary salts. Therefore it is supposed that the white bands formed are chiefly composed of the secondary calcium phosphate.

Outer Electrolyte and the Effect of Its Concentration. A sol was made by mixing 0.75 N acetic acid with an equal volume of sodium silicate solution ($d = 1.06$) and as much of calcium chloride was added to the sol as to become 0.1% in concentration. After the sol set to a gel, secondary sodium phosphate solutions of various concentration were poured on the gel. The experimental results are given in Table 5.

Table 5.* Inner electrolyte: $CaCl_2$ 0.1%.

Conc. of outer electrolyte Na_2HPO_4 (%)	Number of bands formed.
8.74	13
5.82	11
2.91	9
1.96	4
0.87	1

In this case, as much of the sol was taken as to fill to a height of 8 cm. of a test-tube of 1 cm. in inner diameter. The more concentrated sodium phosphate solution gives the more closeness of the bands and the more number of the bands.

Calcium chloride solutions of 5 to 30% were poured on the gel which was prepared in the same manner as the above and contains 0.5% of secondary sodium phosphate. In any case, the clear rhythmic precipitate was produced. The relation between the concentration and number of formed bands is given in Table 6.

Table 6.* Inner electrolyte: Na_2HPO_4 0.5%.

Conc. of outer electrolyte $CaCl_2$ (%)	Number of bands formed.	Remarks
30	8	These three agree completely and no difference is recognized among them.
25	8	
20	8	
15	8	The bands were close in proportion to the concentration of outer electrolyte.
10	8	
5	7	

In the case where the calcium chloride solutions of higher concentrations than 20% were used, no difference was recognized in the closeness and the total number of bands. This was a characteristic result. When the concentration was lower than 15%, the total number of formed bands was large in the case of the highly concentrated outer electrolyte, and

consequently the closeness of bands increased. This is a common rule in the formation of rhythmic precipitate.

Next, the effect of diffusion of different electrolytes into the fixed inner electrolyte was scrutinized. At first, primary potassium phosphate, secondary and tertiary sodium phosphate solutions of an equal concentration were respectively allowed to diffuse into silicic acid gels which were made from a sodium silicate solution ($d = 1.06$) and an equal volume of 0.75 N acetic acid, containing calcium chloride.

According to the experiment with gelatine gel, when the primary salt is allowed to diffuse in, no rhythmic precipitate is formed. In the silicic acid gel, there are the substances which act as a buffer solution on the hydrogen ion concentration. Therefore, it may form a rhythmic precipitate. When the primary salt was diffused, as a matter of course, the bands were formed at large intervals and the number of formed bands also was extremely small.

The diffusion of secondary sodium phosphate gave the most typical rhythmic precipitate, as already described. With tertiary sodium phosphate the rhythmic precipitate was formed, but the silicic acid gel was gradually peptized by the added solution of strong alkaline. On the other hand, the bands of calcium phosphate which had once been formed, received no effect by the alkalinity of the solution and remained unchanged, though they fell down slowly by their own weight to the level where there was still unpeptized gel. In the part where the peptization had not yet occurred, the rhythmic precipitate was successively formed, so that those bands piled up one after another.

Solutions of chloride, bromide, iodide and nitrate of calcium of the equal concentration made respectively diffuse into gels containing sodium phosphate as the inner electrolyte; the rhythmic precipitates were formed at the same distances and closeness, and scarcely any essential difference was found among them.

Effect of the Concentration of Gels. The acetic acid solution of an adequate concentration was added so as to be roughly $p\mathrm{H} = 6$ to the sodium silicate solutions of an equal volume, whose densities were respectively 1.06, 1.08 and 1.10. In any cases of the gels, the formation of the rhythmic precipitates could be observed. In the gel from the silicate solution of the density of 1.10, each stratum of precipitate somewhat blurred on either face and hardly grew into a clear band. Accordingly, the gels of as low concentrations as possible, are adequate for the present purpose of producing the rhythmic precipitate.

Effect of the Presence of a Third Substance. It was already known that the presence of a certain substance in the gel indifferent to the precipitation reaction, often had an effect on the formation and the properties of rhythmic bands. Hatschek, moreover, pointed out that in formation of the rhythmic precipitate of calcium phosphate in gelatine, some marked abnormalities were caused by the kinds of gelatine and impurities in it. The present author mixed the solutions of cane sugar, glucose, urea, potassium bromide and common salt, with the outer electrolyte in order to examine their effect as the third substance. As much of secondary sodium phosphate was added as to become 0.4% in concentration, to the sol which was made by mixing a sodium silicate solution ($d = 1.06$) and an equal volume of 0.75 N acetic acid. After the gel set firmly, the solution of outer electrolyte was put on it which had been prepared by mixing an equal volume of 2 mol calcium nitrate solution with cane sugar (1 and 2 mol solution), glucose (1 and 0.5 mol solution), urea (1 and 0.5 mol solution), sodium chloride (1 mol solution), and potassium bromide (1 mol solution), respectively. Pringsheim[6] states that when two salt solutions diffuse into a gel in opposite directions the reaction does not proceed beyond a thin film if the solutions are isotonic. A hypertonic solution continues to diffuse into a hypotonic and any precipitate formed is deposited in the latter. In accord with this idea, indifferent substances are often added to the solution on the top of the gel in order to ensure reaction below the gel surface. In the present case, however, when a third substance is added to the outer electrolyte, the increase in the diffusion velocity, which is determined by the osmotic pressure of the electrolyte will be very small, so that the effect on the formed rhythmic precipitate is negligible.

Next, the effect of a third substance added to the inner electrolyte was tested. The solution of a third substance was mixed with acetic acid solution to obtain a 0.8 N acetic acid solution and an equal volume of sodium silicate solution ($d = 1.06$) was poured into it. Then as much of secondary sodium phosphate was further added to the mixture as to be 0.4% in concentration. After gelatinized this sol to a firm gel, 2 mol solution of calcium nitrate was added to diffuse into it. When some organic compound (cane sugar, glucose and urea) was added as the third substance, at first, the bands were somewhat closer, but later rather thinner than those in the cases without the addition of the third substances.

(6) *Z. physik. Chem.*, **17** (1895), 473.

When, however, potassium iodide or bromide for instance, was added in the inner electrolyte (0.3 mol in the gel), some different results have been obtained. The first three or four bands could be produced although, whose particles were coarse, while those lower than the fourth or fifth bands composed of so coarse particles, that no distinct bands could be observed. The fact may be explained as follows. When an organic matter such as cane sugar, is added, the outer electrolyte is checked to diffuse into the gel by the osmotic pressure of the substance in the gel. Therefore, the concentration of the diffusing electrolyte inside the gel suffers a sharp gradient, so that the bands will deposit relatively close in the part contacting the diffusing solution, and afterward more thinly than the case where no third substance is added. The abnormalities caused by the presence of inorganic salts may be imputed to the fact that calcium phosphate has generally high solubility in the solutions of some other salts. An excess of the diffusing ion is readily brought forth in the vicinity of the part contacting the diffusing agent, so that the bands are formed. But tolerably deep inside of the gel, the minute change of solubility has a great effect on the velocity of separation of the precipitate. In the case of a high solubility, the separation of the precipitate is slow, and their particles are coarse; accordingly, the precipitate will deposit in abnormal bands.

Effect of Aging. Scott Blair, for the first time, reported that the rhythmic precipitate of silver chromate in a gelatine gel was greatly effected by the aging of the gel before superimposing the diffusing electrolyte.[7] The present author ascertained that this change of gel by the age was not really caused by the change of the structure of the gel.[8] Koenig,[9] on the other hand, advocated the effect of aging even in silicic acid gels, and reported that the abnormal bands were brought forth in an aged gel. But it was already mentioned that the normal rhythmic precipitate of copper chromate could be formed in a gel, which had elapsed a very long time.[8] It seemed, therefore, that the aging has no effect on bands in the case where there is no mutual action between the gel and inner electrolyte, especially in silicic acid gels. This view was confirmed by the rhythmic precipitates of calcium phosphate. The experiments have been conducted as follows. Five c.c. of a 0.5 mol sodium phosphate solution was added to 100 c.c. of a sol, which had been prepared by mixing sodium silicate solution ($d = 1.06$) and an equal volume of 0.75 N acetic

(7) *Phil. Mag.*, **49** (1925), 90.
(8) Isemura, this Bulletin, **8** (1933), 108.
(9) *J. Phys. Chem.*, **24** (1920), 466.

acid, and the mixture was separated into 12 test-tubes and let gelatinized. These test-tubes were kept in a thermostat at 25°C. and an equal volume of 0.5 mol calcium nitrate solution was poured on gels at 1, 3, 12 hours, 1, 2, 3, 4, 5, 9, 10, 12 and 15 days respectively after the setting of the gel. All these test-tubes made quite the same rhythmic precipitate, and cannot be noticed any difference among them. Thus the aging effect, generally, is not observed, provided the inner electrolyte does not react with the gel.

Summary.

(1) The formation of rhythmic precipitate of calcium phosphate in a silicic acid gel was described.

(2) The formation of this rhythmic precipitate was strongly affected by the hydrogen ion concentration of the gel.

(3) The effects of the concentrations of inner and outer electrolytes, and gel on this rhythmic precipitate, were studied.

(4) When the concentration of the inner electrolyte ($CaCl_2$), was sufficiently great, no diffusion of the outer electrolyte into the gel took place but reversely calcium salt diffuse into the outer electrolyte solution and dendrities were formed in the outer solution.

(5) The effect of the existence of a third substance in the gel and in the diffusing electrolyte, were also investigated. The existence of it in a diffusing electrolyte had almost no influence but the existence in a gel had some effects, especially in the case where bromide and iodide of potassium were used as the third substance.

In conclusion the author expresses his hearty thanks to Prof. J. Sameshima of the Tokyo Imperial University for his kind advices throughout the work.

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On the Composition of "Akebi" Seed Oil.

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(Received June 27, 1938.)

In Japan, "Akebi" seed oil is used for food locally in Iwate Prefecture, and the analytical constants of this oil have hitherto been reported by S. Uchida.[1] This oil has a peculiar characteristic, which is of extraordinarily high Reichert-Meissl value, but we have not any researches on the composition of it. The present authors have made a thorough examination on this oil, with the results that palmitic, stearic, oleic and linoleic acids were separated, and the presence of acetic acid was also confirmed.

I. The Seed Oil of "Mituba Akebi" (*Akebia lobata*, Decne.). The fruits of "Mituba Akebi", which ripen in October, are shown in Fig. 1. They contain numerous small black seeds as shown in Fig. 2, and 50 grains of the latter weigh 1.3 g. on the average.

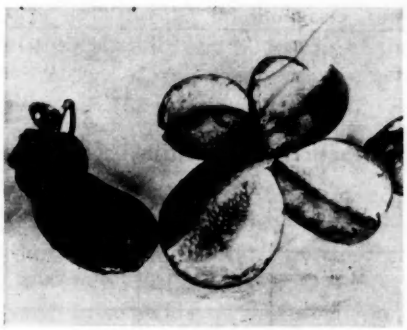

Fig. 1. Fruits of "Mituba Akebi."

Fig. 2. Seeds of "Mituba Akebi" (life-size).

The seeds (350 g.) were ground, and by ether extraction, light yellow oil (97 g.) was obtained. The oil had the following characteristics: n_D^{20} 1.4652, d_4^{20} 0.9326, acid value 6.6, saponification value 254.9, iodine value

(1) *J. Soc. Chem. Ind.*, **35** (1916), 1091; *J. Soc. Chem. Ind., Japan*, **19** (1916), 33.

78.6, and Reichert-Meissl value 49.3. The sample oil (76 g.) was saponified and after the removal of unsaponifiable matter (0.7715 g.) by ether extraction, the soap solution was decomposed with dilute hydrochloric acid and mixed fatty acids (57 g.) were obtained.

(1) *Water soluble part.* The acidic solution, obtained by the decomposition of soap solution, was concentrated under reduced pressure after neutralisation. The concentrated solution was acidified, saturated with common salt, and extracted with large quantity of ether. The extracted substance had an irritative odour like acetic acid, and distilled at 108–114° under the ordinary pressure. The distilled substance was converted into *p*-bromophenacyl ester, two crystallisations from 75% ethyl alcohol gave an ester, m.p. 85.5–86°, which showed no depression of melting point when mixed with pure acetice acid *p*-bromophenacyl ester.

(2) *Water insoluble fatty acids.* The mixed fatty acids obtained as mentioned above formed a white semi-solid, which had n_D^{40} 1.4521, neutralisation value 203.3, iodine value 91.2. The mixed fatty acids (53 g.) were separated by the lead salt–alcohol method of Twitchell into solid and liquid portions as shown in Table 1.

Table 1.

	Yield	Neutralisation value	Iodine value
Solid acids	17.17 g. 32.4%	213.9	22.5
Liquid acids	67.6%	199.3	120.2

The solid fatty acids (15 g.) were fractionally redistilled as shown in Table 2.

Table 2.

Fraction	B.p./4 mm.	Yield (g.)	M.p.	Neutral. value	Iodine value
1	−175°	4.6	57.7–58.6°	217.4	7.6
2	175–180°	5.2	54.5–55.8°	215.2	19.4
3	180–184°	4.1	43.5–45.0°	209.0	41.3
Residue		0.8			

As the results of careful examinations of fractions 1 and 3, the authors isolated a large quantity of palmitic acid, and a small quantity of stearic acid.

The liquid acids obtained by the lead salt–alcohol method were converted into methyl esters and fractionally distilled as shown in Table 3.

Table 3.

Fraction	B.p./4 mm.	Yield (g.)	n_D^{20}	Saponif. value	Iodine value
1	176°	3.3	1.4541	190.2	112.2
2	176–177°	19.9	1.4545	189.1	116.7
3	177°	5.1	1.4550	189.4	117.5
Residue		1.1			

The saponification value of each fraction in Table 3 showed the non-existence of fatty acids having carbon numbers other than 18. In the fraction 2, oleic and linoleic acids were detected, as dihydroxystearic acid and tetrabromostearic acid respectively.

From the result of the above analysis, the mixed fatty acids of "Mituba Akebi" seed oil seemed to consist of the following composition: palmitic acid 23%, stearic acid 2%, oleic acid 53% and linoleic acid 22%.

II. The Seed Oil of "Itutuba Akebi" (*Akebia quinata*, Decne.). The seeds of "Itutuba Akebi" are comparatively larger than the seeds of "Mituba Akebi", and 50 grains of them weigh 4.03 g.

210 g. of the seeds were crashed, extracted with ether, and dark green oil (41 g.) was obtained. It had the following properties: n_D^{20} 1.4667, d_4^{20} 0.9354, acid value 2.0, saponification value 259.5, iodine value 77.3, Reichert-Meissl value 44.8, unsaponifiable matter 2.6%.

In the oil (28 g.) the existence of acetic acid was confirmed in the same way as the seed oil of "Mituba Akebi". The mixed fatty acids formed a dark green semi-solid, and their characteristics (n_D^{40} 1.4523, neutralisation value 205.1, iodine value 89.1), resembled very much those of the mixed fatty acids of "Mituba Akebi".

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